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ORIGINAL PAPER

# Determination of organic micro-pollutants such as personal care products, plasticizers and flame retardants in sludge

**Xijuan Chen · Kai Bester**

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**Abstract** In this study, a method for the determination of organic micro-pollutants, i.e. personal care products such as synthetic musk fragrances, household bactericides, organophosphate flame retardants and plasticizers, as well as phthalates in sludge, has been developed. This method is based on lyophilisation and accelerated solvent extraction followed by clean-up steps, i.e. solid phase extraction and size exclusion chromatography. The determination is performed by gas chromatography coupled to mass spectrometry. Stable isotope-labelled compounds such as musk xylene (MX $D_{15}$), tri-*n*-butylphosphate (T*n*BP $D_{27}$) and triphenylphosphate (TPP $D_{15}$) were used as internal standards. Recovery rates were determined to be 36–114% (with typical relative standard deviation of 5% to 23%) for the target compounds. The limit of detection was 3–30 ng $g^{-1}$, and the limit of quantification was 10–100 ng $g^{-1}$ dry matter.

**Keyword** Personal care products · Musk fragrances · Triclosan · Household bactericides · Organophosphates · Phthalates

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## Introduction

Sewage sludge is produced in waste water treatment while removing compounds causing oxygen demand ($BOD_5$) from the waste water. Thus sludge contains high concentrations of organic matter, nutrients (nitrogen and phosphorous) and lipophilic organic micro-pollutants from the waste water. Some countries such as the Nordic countries prefer to use the nutrients in agriculture (re-cycling of sludge), while some others (e.g. Switzerland) have decided to incinerate all sludges as they prioritised to destroy all micro-pollutants. The majority of countries do a case by case decision depending on the concentrations of organic micro-pollutants and heavy metals. Thus a sound basis for analysing organic micro-pollutants in sludge is necessary to make sure that only sludge with low contaminations is used for re-cycling in agriculture. Established methods are usually single or group specific such as the methods used to analyse PAHs or PCBs [1, 2]. Often the analytical protocols are similar to those established for sediments with a high load of TOC.

The compounds included in this study were synthetic musk fragrances (musk xylene, musk ketone, HHCB, AHTN, HHCB–lactone), an antimicrobial and its metabolite (triclosan, triclosan–methyl), organophosphate flame retardants and standing for organophosphate-plasticizers (tri-*iso*-butylphosphate (T*i*BP), tri-*n*-butylphosphate (T*n*BP), tris-(2-chloroethyl) phosphate (TCEP), tris-(2-chloro-*iso*-propyl) phosphate (TCPP), tris-(dichloro-*iso*-propyl) phosphate (TDCP) and triphenylphosphate (TPP)) and the phthalate (di(2-ethylhexyl) phthalate (DEHP); Table S1). Some of these compounds have been discussed in national as well as developing EU laws on sludge as maker compounds for the re-use of this material [3, 4].

Synthetic musk fragrances are compounds used as low cost fragrances in soaps, perfumes, air fresheners, deter-

gents, fabric softeners and other household cleaning products. There are four synthetic musk fragrances accounting for 95% of the used musk. These are two polycyclic compounds (HHCB and AHTN) as well as the nitro-musks (musk xylene and musk ketone). These compounds have been detected in surface water [5, 6], in waste water [7–9] and in sewage sludge [10–12]. HHCB–lactone is the primary metabolite of HHCB (Table S1). The ratio HHCB versus its metabolite HHCB–lactone has been used to detect transformation processes of this fragrance. During the sewage treatment process, about 10% of HHCB is transformed to HHCB–lactone, which has been reported for balance assessment for polycyclic musk fragrances in a German treatment plant by Bester [8]. Reviews of several analytical strategies for the analysis of musks in sludge have been described by using accelerated solvent extraction (ASE), supercritical fluid extraction, Soxhlet extraction and liquid–liquid extraction, all of them in combination with gas chromatography–mass spectrometry (GC–MS) [13–15].

Triclosan (Table S1) is an antimicrobial agent, which is widely used in personal care products such as toothpaste, soaps, deodorants, cosmetics and skin care lotions as well as other consumer goods. Approximately 1,500 t is produced annually worldwide, and approximately 350 t of those is applied in Europe [16]. Triclosan–methyl (Table S1) is a transformation product of triclosan. These two compounds have been identified in the environment by several investigators [16–21], whereas bioaccumulation and toxicity have been studied by Orvos et al. [22], Coogan et al. [23] and De Lorenzo et al. [24]. Analytical methods for analysing antimicrobials in sludge by using GC–MS and liquid chromatography–MS have been reviewed by Peck [13].

The organophosphates included in this study were chlorinated alkylphosphates such as TCPP, TCEP and TDCP, which are mostly used as flame retardants in polyurethane. Additionally, non-derivatised alkylphosphates such as the two isomers of tri-butylphosphate (T*n*BP and T*i*BP) and TPP, which are used as plasticisers, were studied as well. Because of their relatively low cost, organophosphates especially TCPP have become the most widely used class of flame retardants [25]. These compounds are washed off from the equipped items during cleaning; the cleaning water will be discharged to the sewer and thus reach waste water treatment plants, as discussed by Fries and Puttmann [26] as well as by Meyer and Bester [27]. Additionally, these organophosphates have been detected in indoor air as well as in indoor dust by Sanchez et al. [28] and García et al. [29]. Only a few analytical procedures to determine organophosphates in sludge or sediment with high TOC content have been described [30, 31].

DEHP is one of the most widely used plasticizers. It is used mainly for making PVC soft and pliable. This plasticizer is eluted into waste water by washing and cleaning processes of the respective materials; it is assumed to have ecotoxic (endocrine disrupting) effects to aquatic organisms [32]. Because of the relatively high lipophilicity of this phthalate, sorption is the main process relevant for elimination in sewage treatment plants. Typical concentration of DEHP in sludge was found to be ranging from 10 to 100 μg $L^{-1}$ by Fromme et al. [33]. Extraction methods in combination with GC–MS have been described by Sablayrolles et al. [34] and Aparicio et al. [35].

The main objective of the research presented in this paper was to develop and validate an analytical multimethod to determine different classes of organic micropollutants such as personal care products, plasticizers and flame retardants and phthalates in sludge.

## Experimental section

### Materials

AHTN, triclosan, musk xylene, musk ketone and DEHP were purchased from Ehrenstorfer (Augsburg, Germany) as pure compounds with purities being ≥99% according to the supplier. Pure standards of HHCB–lactone as well as HHCB were obtained from International Flavours and Fragrances (IFF, Hilversum, Netherlands). Triclosan–methyl was synthesised from triclosan by methylation with trimethylsulfonium hydroxide solution (Macherey-Nagel, Dueren, Germany) at 40°C [20].

TCPP and TDCP were obtained from Akzo Nobel (Amersfoort, the Netherlands). These compounds were used without further purification. The technical TCPP gives three peaks in the ratio 9:3:1. In this study, only the main (first eluting) isomer was used for determination. T*n*BP, T*i*BP, TPP and TCEP were purchased from Sigma-Aldrich (Steinheim, Germany). Ethyl acetate, acetone, cyclohexane and methanol were used in analytical grade (p.a.) quality, while toluene and *n*-hexane were used in residue grade (z.R.) quality. All solvents were purchased from Merck (Darmstadt, Germany).

#### Internal standards

The internal standard musk xylene $D_{15}$ was used to quantify the musk fragrances musk xylene, musk ketone, HHCB, AHTN, triclosan–methyl and DEHP as it elutes in the same fraction as these compounds, while T*n*BP $D_{27}$ was used to quantify T*i*BP, T*n*BP, TCEP and TCPP, and TPP $D_{15}$ was used in this experiment to quantify triclosan, HHCB–lactone, TDCP and TPP. Musk xylene $D_{15}$ and T*n*BP $D_{27}$ were obtained from Ehrenstorfer (Augsburg,

Germany); TPP $D_{15}$ was synthesised from $D_6$ phenol and phosphoroxychloride. These internal standards were chosen as they give undisturbed signal and also do not undergo any reaction themselves [36].

## Analytical method

The sample preparation scheme is shown in Fig. 1: After sampling, the sludge samples were immediately frozen at −27 °C overnight. "Dried sludge" such as produced at waste water treatment plants contains about 70% water; thus drying is essential to provide good wettability of the sludge with organic solvents. The frozen sub-samples of 40 g wet weight were then lyophilised overnight at 2 mbar and −46 °C using an ALPHA 1-2/LD (Christ, Osterode am Harz, Germany). The 4–6 g lyophilised sludge samples was blended with about 10 g diatomaceous earth (acid-washed obtained from MP Biomedicals, Solon, OH, USA) and homogenised in a mill (IKA A11 BASIC, Staufen, Germany) to a fine powder. The homogenates were then transferred into a 33-mL stainless steel ASE cell and extracted successively with ethyl acetate (ASE 200, Dionex, Sunnyvale, USA). After adding an aliquot of 500 µl internal standard solution (IS; containing 500 ng $D_{15}$ musk xylene, 500 ng TPP $D_{15}$ and 500 ng T*n*BP $D_{27}$), the extract was concentrated to 1 mL by a Büchi Synchore multiport concentrator (Büchi, Essen, Germany) at 80 °C and 70 mbar.

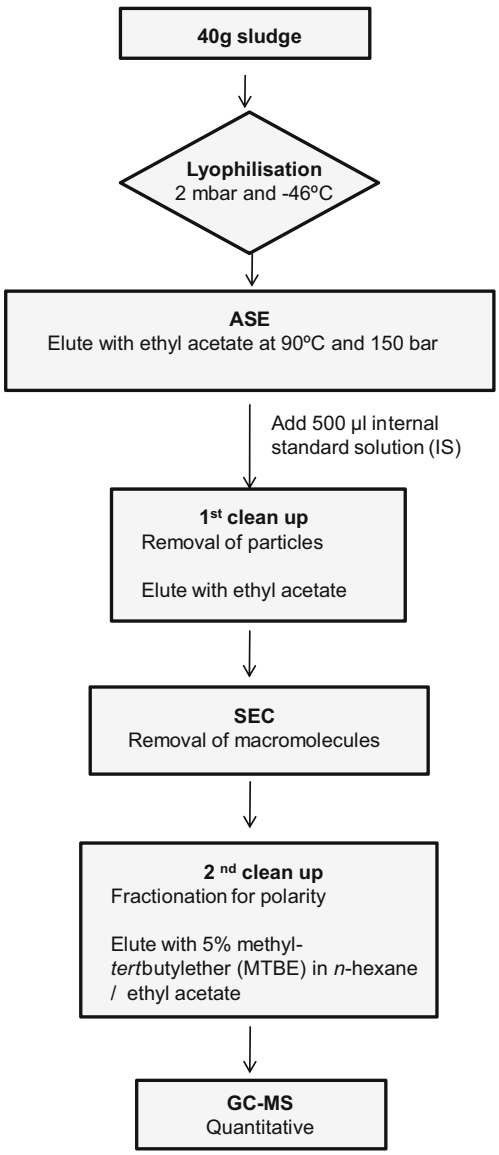


**Fig. 1** Sample preparation scheme

The resulting extracts were cleaned up with silica solid phase extraction (SPE) cartridges. This step is primarily protecting the next step (size exclusion chromatography (SEC)) from too many particles as well as very polar compounds. It was performed by packing 1 g of silica (silica 60 obtained from Merck, Darmstadt, Germany, pre-dried at 105 °C) into a glass column (60 mm long, 12 mm ID) with two PTFE frits on the top and bottom of silica. The silica column was conditioned with 12 mL *n*-hexane before use and eluted with 12 mL ethyl acetate after loading the samples.

The resulting extracts were again concentrated by a Büchi Synchore multiport concentrator and successively injected into an SEC system (GPC-Basix, purchased from LC-Tech, Dorfen, Germany) equipped with a glass column ID: 2.5 cm, length 30 cm, packed with 50 g SX-3 (Bio-Rad, Hercules, CA, USA). The mobile phase was cyclohexane and ethyl acetate (1:1, *V*/*V*) and the flow rate was 5.0 mL $min^{-1}$. The solvent eluting in the first 19.30 min (97.5 mL) containing macro-molecules was drained to waste, while the fraction 19.30–30.00 min (52.5 mL) containing the analytes was collected [37]. The samples were finally transferred into toluene by adding 10 mL toluene and condensing to 1 mL. Thus, macro-molecules were separated as they are eluted in the first fraction, while sulphur, etc. are separated from the target compounds as they are eluted after the analyte fraction.

The resulting extracts were then fractionated for polarity on silica 60 using 12 mL 5% methyl-*tert*butylether in *n*-hexane (first fraction) and 12 mL ethyl acetate (second fraction) successively as eluents. The musks, triclosan–methyl and DEHP were eluted in the first fraction, while T*i*BP, T*n*BP, TCEP, TCPP, TDCP and TPP as well as triclosan and HHCB–lactone were eluted in the second fraction according to their polarity. These fractions were transferred into toluene as described above and finally analysed by GC–MS detection.

The GC–MS system was a DSQ purchased from Thermo, Waltham, USA. The GC was equipped with a programmable temperature vapouriser (PTV) injector. The

PTV (1 µl injection volume) was operated in PTV splitless mode. The injection temperature of 115 °C was held for 3 s; it was successively ramped with 12 to 280 °C $s^{-1}$ for the transfer of the analytes into the column. This temperature was held for 1.3 min. The injector was then ramped with 1 to 300 °C $s^{-1}$ (open split), which was held for 7 min as a cleaning phase.

The GC separation was performed with a DB-5MS column (J&W Scientific), L was 15 m, ID was 0.25 mm, and film thickness was 0.25 µm. The oven temperature programme started at 100 °C (hold, 1 min) and was then ramped with 30 to 130 °C $min^{-1}$ and successively with 8 to 220 °C $min^{-1}$. Finally, the baking temperature was reached by ramping the oven with 30 to 280 °C $min^{-1}$, which was held for 7 min.

The transfer line was held at 250 °C, which is sufficient to transfer all compounds from the GC into the MS as the vacuum builds up in the transfer line. The ion source was operated at 230 °C. Helium (4.0) was used as carrier gas with a flow rate of 1.3 mL $min^{-1}$. All compounds were detected by means of their mass spectral data and retention times as shown in Table 1.

Calibrations were performed as a multi-step internal standard calibration. A stock solution was produced by dissolving 20 mg of the target compounds into 100 mL acetone. This stock solution was stored at 4 °C in the dark. The weight of this flask was controlled before and after each operation. Calibration standards (3, 10, 30, 100, 300, 1,000, 3,000 and 10,000 ng $mL^{-1}$ in toluene) were made by serial dilution of the stock solution. The calibration standards contained the internal standards with a concentration of 100 ng $mL^{-1}$. The calibration curve was calculated by using a weighted ($1/X$) linear regression.

## Results and discussions

Extracting organic compounds from sludge is optimised between extracting as much as possible of the target compound and as little as possible of the organic matter of the sludge, as the latter will be corrupting the GC or either one of the following steps.

Three experiments were performed to determine the optimal conditions for the accelerated solvent extraction in the method development and method validation after it had been decided to focus on ethyl acetate as an extractant:

1. A temperature optimisation, which was compared to total and destructive extractions
2. Validation from an artificial blank material to determine potential concentration dependency of the recovery rate as well as blank problems
3. Validation from a spiked sludge to determine recovery rates by different means as well as gain insight on realistic precision

### Optimisation of extraction temperature

Temperature is the most important parameter used in ASE extraction. ASE operates at temperatures above the normal boiling point of most solvents, using pressure to keep the solvents in the liquid phase during the extraction process. As the temperature is increased, the viscosity of the solvent is reduced, thereby increasing its ability to wet the matrix and solubilise the target analytes. However thermal degradation of the solvent or the sample might occur at higher temperatures [38, 39]. In this study a temperature range from 50 to 150 °C was tested for the optimisation of

**Table 1** Retention times and selected mass fragments for the determination of the respective compounds using a DB-5 column

| Compound | RT (min) | Quantifier mass (amu) | Verifier mass (amu) |
|---|---|---|---|
| OTNE | 5.96 | 191 | 219 |
| Musk xylene | 8.12 | 282 | 297 |
| Musk ketone | 9.50 | 279 | 294 |
| HHCB | 8.03 | 243 | 258 |
| AHTN | 8.14 | 243 | 258 |
| HHCB–lactone | 11.73 | 257 | 272 |
| Triclosan | 11.07 | 288 | 290 |
| Triclosan–methyl | 11.30 | 302 | 304 |
| T*i*BP | 4.37 | 155 | 211 |
| T*n*BP | 5.80 | 155 | 211 |
| TCEP | 7.19 | 249 | 251 |
| TCPP | 7.46 | 277 | 279 |
| TDCP | 13.35 | 379 | 381 |
| TPP | 13.88 | 325 | 326 |
| DEHP | 14.60 | 149 | 167 |

extraction. For the extraction of organic micro-pollutants, one sub-sample of homogenised dried sludge was extracted by ASE with temperatures of 50, 70, 90, 110, 130 and 150 °C, each followed by first clean up, SEC and the second clean up as described above. In the end the samples were measured by GC–MS. The highest concentration of HHCB, AHTN, triclosan and HHCB–lactone was found from the 70 and 90 °C extractions, which is shown in Fig. 2. The increased concentration of HHCB–lactone found at 130 °C was interpreted as result of an oxidation of HHCB under these conditions. Therefore, 90 °C was selected as the extraction temperature because of the better extraction efficiency proved here and suggested references [38, 39]. As a control, total extractions with acetone and acidified methanol at 150 °C were performed. These did not give higher concentrations than those with ethyl acetate at 90 °C and 150 bar.

### Method validation from artificial blank material (manure/soil) recovery rates and working range

These experiments were performed to determine whether the recovery rate was dependent on the concentration or not. The working range was considered to range from the lowest to the highest concentrations for which the same recovery rates were obtained. A blank material, which contains similar TOC and ammonia content as sludge but no analytes, was produced by mixing manure from organic farming with soil (1:1). Various concentrations of the standard were spiked into the dried homogenized material. The spiked sub-samples were transferred into ASE cells, which were extracted with the method described above. Table 2 shows the recovery rate and its working range determined from the spiked artificial blank material. Figure S1 shows the recovery rate of triclosan as the function of concentration. The recovery rates for all compounds are independent on the concentrations (Table 2). It was also demonstrated that no other peaks (e.g. from decomposition/ pyrolysis) of biogenic material that could be mistaken for the analytes occurred from such matrices.

### Method validation from spiked sludge samples (LOQ)

These recovery experiments were carried out by providing six homogeneous sub-samples from one sludge sample and each was spiked with 125 µl of the stock solution (200 µg $mL^{-1}$). Two other sub-samples were left unspiked as comparison. They were lyophilised and then extracted at 90 °C and 150 bar. The following sample preparation, extraction and clean up were identical to the procedures described above. For this study, dewatered digested sludge of an urban waste water treatment plant with 450,000 population equivalents, operating BOD, nitrogen and phosphorous removal was used. The sludge had a water content of 90% before lyophilisation. The mineral content of the total solid content was 33%. The concentrations of the target compounds in this sludge before and after spiking are shown in Table 3. Figure 3 shows the chromatographic characterisation of TCPP in one unspiked sludge sample (18,400 ng $g^{-1}$).

Since the standard deviation from this six spiked samples was low and no outlier was identified, all results were averaged. The mean recovery rates were 36–114%, and the relative standard deviations were 5–23% (Table 3), depending on the respective compounds. The lower recovery rates of musk xylene and musk ketone were possibly due to the occurrence of biotransformation of the nitro-musks during the sample preparation process [40, 41]. The limit of detection was taken as signal-to-noise ratio 3:1, and the limit of quantification (LOQ) was defined as signal-to-noise ratio 10:1, which was calculated by the Xcalibur software (Thermo, Waltham, USA) for the respective SIM chromatograms of the standard calibration (Table 3). The thus obtained LOQs are in the same range as the lower end of the working range (see above, Table 2). Comparable results were obtained by Bester [30] who used a similar procedure

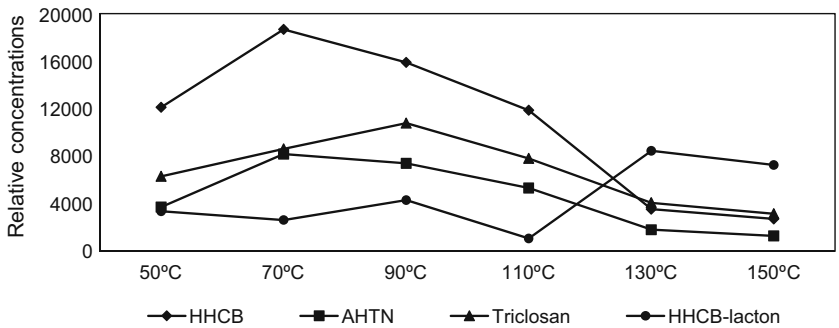


**Fig. 2** Relative concentrations of HHCB, AHTN, HHCB–lactone and triclosan obtained by ASE extractions of sludge homogenates at different temperatures

**Table 2** Recovery rate and working range determined by the artificial blank material

| Compound | Working range ($ngg^{-1}$) | RR (%) | RSD (%) |
|---|---|---|---|
| OTNE | 30–10,000 | 73 | 26 |
| HHCB | 300–10,000 | 87 | 13 |
| Triclosan | 30–10,000 | 88 | 9 |
| TiBP | 30–10,000 | 77 | 6 |
| TCEP | 10–10,000 | 70 | 11 |

but utilised a Soxhlet extraction to determine polycyclic musk fragrances and TCPP in waste water treatment plant.

## Stereoisomer separation

Stereoisomer-specific determination often gives in-depth insights into ongoing processes; however, this analytical technique is more vulnerable to matrix than conventional analysis, as the respective columns have lower temperature limits. Thus, stereoisomer-specific determination requires better sample clean ups. In this study, it was tested whether the developed sample clean up is suitable also for stereoisomer determination. The gained extracts were used for stereoisomer separation of OTNE. OTNE has two chiral centres; thus enantiomers and diastereomers may occur. The synthesis of this compound is not stereoselective; thus both kinds of stereoisomers are expected in the product [42].

Stereoisomer separation was performed on a heptakis-(2,3-di-*O*-methyl-6-*O*-*t*-butyldimethyl-silyl)-β-cyclodextrin (Hydrodex 6-TBDMS) column (Macherey-Nagel, Düren, Germany). This column is able to separate enantiomers as well as diastereomers of compounds such as polycyclic musks [15], but for OTNE only two major peaks were observed (Fig. 4). Thorough temperature programme and gas flow optimisation were performed and resulted in a temperature programme of 90 °C [1 min] → 10 °C $min^{-1}$ → 115 °C [70 min] → 10 °C $min^{-1}$ → 200 °C [30 min] at a constant flow of 1.2 mL $min^{-1}$ helium gave the best separation from the production impurities. However, only two main stereoisomers could be separated. It is thus currently unknown whether the achieved separation separates the enantiomers or diastereomers of OTNE. However, in this study, it could be demonstrated that the extracts were clean enough to give reliable stereoseparation. A multitude of standards and sludge samples were analysed in one sequence with no change of chromatographic performance. Thus this multi-method is capable to perform sample clean up for stereoseparations as well as conventional analysis.

**Table 3** Typical concentration of compounds in sludge samples, mean recovery, relative standard deviation (RSD), limit of detection (LOD) and limit of quantification (LOQ)

| Compound | Concentration in unspiked sludge ($ngg^{-1}$) | Calculated concentration in spiked sludge ($ngg^{-1}$) | Determined concentration ($ngg^{-1}$) | Mean recovery rate (%) | RSD (%) | LOD ($ngg^{-1}$) | LOQ ($ngg^{-1}$) |
|---|---|---|---|---|---|---|---|
| OTNE | 3,000 | 10,927 | 6,513 | 60 | 6 | 10 | 30 |
| MX | 80 | 9,200 | 4,300 | 47 | 19 | 10 | 30 |
| MK | 40 | 7,600 | 2,700 | 36 | 23 | 3 | 10 |
| HHCB | 11,800 | 20,300 | 15,700 | 77 | 6 | 3 | 10 |
| AHTN | 1,600 | 8,900 | 6,100 | 69 | 5 | 3 | 10 |
| HHCB–lactone | 800 | 7,900 | 5,200 | 66 | 10 | 3 | 10 |
| Triclosan | 4,400 | 11,700 | 15,600 | 114 | 12 | 30 | 100 |
| Triclosan–Me | 70 | 7,300 | 4,000 | 55 | 10 | 3 | 10 |
| T*i*BP | 100 | 8,100 | 6,200 | 77 | 10 | 10 | 30 |
| T*n*BP | 90 | 7,700 | 4,900 | 64 | 8 | 10 | 30 |
| TCEP | 70 | 11,900 | 7,000 | 59 | 9 | 10 | 30 |
| TCPP | 18,400 | 28,000 | 27,000 | 96 | 8 | 30 | 100 |
| TDCP | 90 | 8,500 | 4,400 | 52 | 8 | 10 | 30 |
| TPP | 400 | 7,600 | 4,300 | 57 | 5 | 3 | 10 |
| DEHP | 8,700 | 17,200 | 15,000 | 87 | 21 | 3 | 10 |

The LOD was taken as signal-to noise ratio 3:1, and LOQ was defined as signal-to-noise ratio 10:1, which was calculated by the Xcalibur software (Thermo, Waltham, USA) for the respective SIM chromatograms of the standard calibration. Mean recovery rates were calculated by the ratio of determined concentration and calculated concentration in spiked sludge

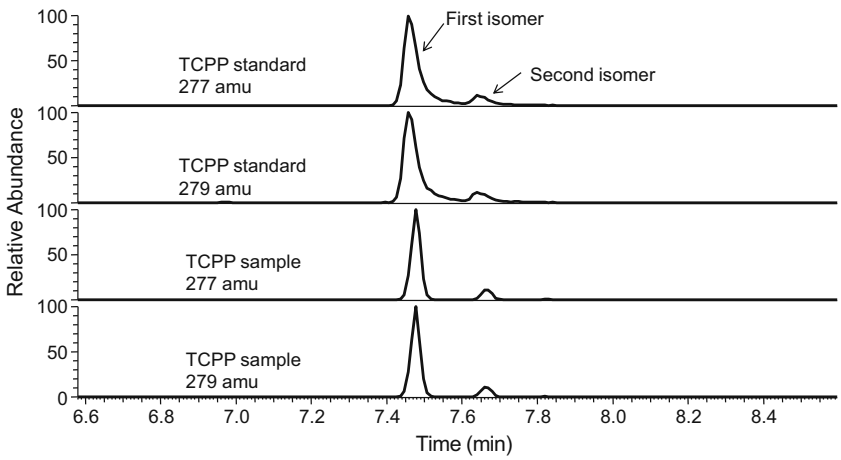


**Fig. 3** Chromatographic characterisation of the organophosphate flame retardant TCPP. The third isomer was not detected as the respective SIM function was aborted before elution of this compound

## Conclusion

A precise multi-method has been developed to analyse musk fragrances, bactericides as well as organophosphates and flame retardants and phthalate by using lyophilisation, ASE in combination with the clean-up steps of SPE, SEC and the detection of GC–MS. The recovery rates obtained from two different recovery experiments performed by two different operators were comparable. In diverse projects, this method has been used to analyse several hundred sludge samples especially in degradation and process studies, for which precision as well as stability of the system were crucial. Though the DSQ–MS needs regular cleaning of the curved prefilter quadrupole after injecting about 100 extracts in duplicate plus calibration standards, the method performed well in routine operations. It is a multi-method that in lots of cases is open to including new analytes. Also the extracts were clean enough to perform stereoseparation. Thus a method was validated, which can be the backbone of future research on organic micro-pollutants in sludge.

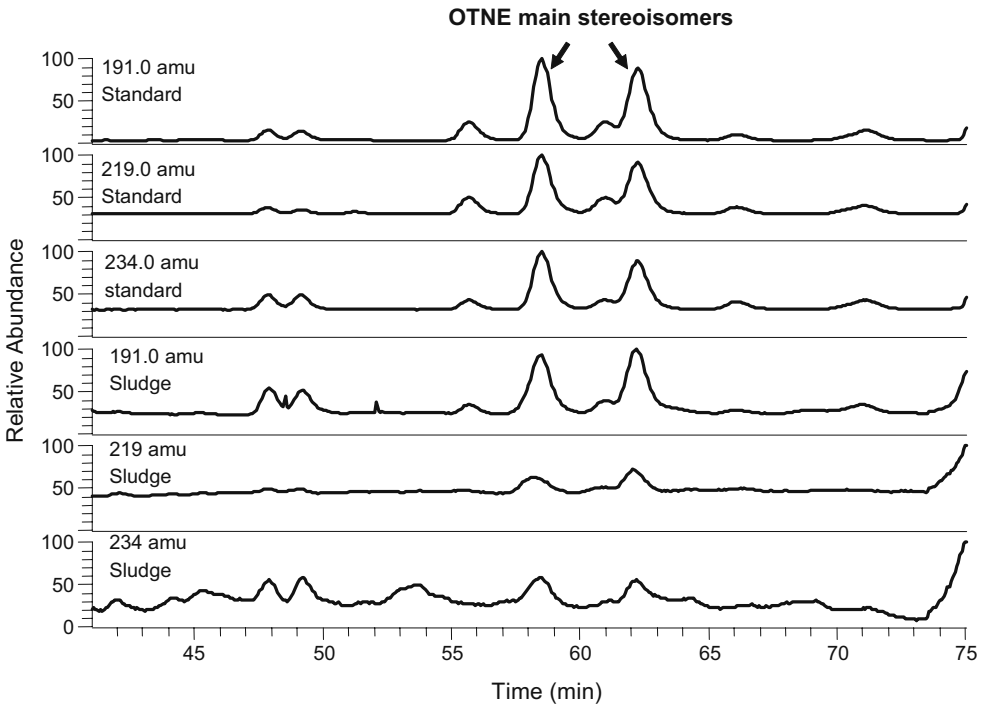


**Fig. 4** Separation of stereoisomers of OTNE on a heptakis-(2,3-di-*O*-methyl-6-*O*-*t*-butyldimethyl-silyl)-β-cyclodextrin (Hydrodex 6-TBDMS®) column. The main stereoisomers were detected at 58.50 and 62.27 min. Temperature programme: 90 °C [1 min] → 10 °C $min^{-1}$ → 115 °C [70 min] → 10 °C $min^{-1}$ → 200 °C [30 min] at a constant flow 1.2 mL $min^{-1}$

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